



# Preparation and characterization of two supramolecular complexes with 5-amino-2,4,6-triiodoisophthalic acid under *N*-donor auxiliary ligand intervention

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## ABSTRACT

Assemblies of 5-amino-2,4,6-triiodoisophthalic acid (H<sub>2</sub>ATIBDC) with Cd(II) and Zn(II) in the presence of *N*-donor auxiliary ligand, 1,4-bis(1,2,4-triazol-1-yl)butane (btb), at ambient conditions yield two new supramolecular complexes, [Cd(ATIBDC)(btb)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 3H<sub>2</sub>O (**1**), and [Zn(ATIBDC)(btb)] $\cdot$ 2H<sub>2</sub>O (**2**). Generally, these two complexes display 1D ATIBDC<sup>2-</sup>-bridged coordination arrays. Distinct extended 3D network architectures are further constructed with the help of weak secondary interactions especially aromatic stacking, halogen bonding, and hydrogen bonding as supramolecular driving forces. It is worthy to mention that halogen bonds (C–I $\cdots$  $\pi$  and C–I $\cdots$ N/O) play important roles in the supramolecular assembly. The pentameric cluster (H<sub>2</sub>O)<sub>5</sub> in **1** assembles into highly ordered helical infinite chains. Complex **2** exhibits the fascinating single-walled tube-like chain structure. It loses crystallinity rapidly in the air and leads to the formation of [Zn(ATIBDC)(btb)] $\cdot$ H<sub>2</sub>O (**2A**). Thermal stabilities and solid state fluorescent properties of complexes **1** and **2A** have been studied.

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## 1. Introduction

The aim of contemporary supramolecular chemistry and crystal engineering is the development of new crystalline materials with various functions and possible applications such as molecular adsorption, magnetism, nonlinear optics, molecular sensing, heterogeneous catalysis, and photoactive materials although the rational design and synthesis of metal–organic frameworks (MOFs) with target structure and function still remains a long-term challenge [1–11]. The construction of supramolecular architectures depends on the combination of several factors, such as the coordination geometry of metal ions, the nature of organic ligands, the use of noncovalent interactions (hydrogen bonding, halogen bonding,  $\pi$ – $\pi$  interactions, or their combination in different ways) and sometimes the reagent ratio [12–15]. So, understanding how these considerations affect metal coordination and influence crystal packing is at the forefront of controlling coordination supramolecular arrays. It has been documented that the geometries of organic ligands play crucial roles in determining the resulted polymeric structures [16].

At present, we are focusing our attention on using iodine-containing 5-amino-2,4,6-triiodoisophthalic acid (H<sub>2</sub>ATIBDC) as the organic moiety to assemble with transition metal ions in the presence of *N*-donor auxiliary ligand, which is based mostly upon the following considerations: (1) Three I atoms in H<sub>2</sub>ATIBDC are potential interaction sites for forming C–I $\cdots$ N/O, C–I $\cdots$ I, or C–I $\cdots$  $\pi$  halogen bonds which may help to extend the linkage into high dimensional supramolecular network due to their specific directional nature and relatively high halogen bonding energy. (2) ATIBDC<sup>2-</sup> is a rigid aromatic dicarboxylate ligand and thus can play the role of a bridging rod. Therefore, a structural prediction of the resulting polymeric complexes may be possible to some extent. Furthermore, due to the presence of aromatic/hetero rings of ATIBDC<sup>2-</sup> and *N*-donor auxiliary ligand in the assembled system, the delicate  $\pi$ – $\pi$  stacking interactions are available to play a significant role in regulating the resulting supramolecular networks. Several novel complexes with the ATIBDC<sup>2-</sup> ligand have been reported [17,18].

We had finished a systematic study focusing on the p-block metal Pb(II) with ATIBDC<sup>2-</sup> ligand [19]. In this paper, we will describe our recent research results of the synthesis, crystallography, and properties of two supramolecular complexes with H<sub>2</sub>ATIBDC in order to further understand the coordination chemistry of H<sub>2</sub>ATIBDC with d<sup>10</sup> metal ions, the roles of three I atoms in the supramolecular assembly. With the introduction of organonitrogen auxiliary

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ligand, 1,4-bis(1,2,4-triazol-1-yl)butane (btb), two interesting supramolecular complexes,  $[\text{Cd}(\text{ATIBDC})(\text{btb})(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$  (**1**) and  $[\text{Zn}(\text{ATIBDC})(\text{btb})] \cdot 2\text{H}_2\text{O}$  (**2**), have been obtained. In this work, we attempt to demonstrate the roles of supramolecular interactions, such as hydrogen bonding and halogen bonding ( $\text{C}-\text{I} \cdots \pi$ ,  $\text{C}-\text{I} \cdots \text{N}/\text{O}$ ), in engineering the resultant crystalline architectures. The pentameric water cluster  $(\text{H}_2\text{O})_5$  in **1** assembles into highly ordered helical infinite chains. Complex **2** exhibits a fascinating single-walled tube-like chain structure and desolvates partly in the air forming  $[\text{Zn}(\text{ATIBDC})(\text{btb})] \cdot \text{H}_2\text{O}$  (**2A**). Solid state fluorescent properties of **1** and **2A** have been investigated.

## 2. Experimental

### 2.1. Materials and characterization

The nitrogenous auxiliary ligand, 1,4-bis(1,2,4-triazol-1-yl)butane (btb), was synthesized according to the literature method [20]. The other reagents were purchased commercially. Elemental analyses (C, H, and N) were carried out on a 240 C Elemental analyzer. FT-IR spectra ( $4000\text{--}400\text{ cm}^{-1}$ ) were recorded from KBr pellet in Magna 750 FT-IR spectrophotometer. Solid state emission spectra were recorded using an F 4500 fluorescence spectrometer. Both the excitation and emission pass width are 5.0 nm. Thermogravimetric analysis (TGA) was taken on NETZSCH STA 409 PG/PC instrument from room temperature to  $800\text{ }^\circ\text{C}$  at a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  in  $\text{N}_2$ . X-ray powder diffraction data were collected at room temperature on a computer-controlled Bruker D8 Advanced XRD diffractometer equipped with Cu  $K\alpha$  monochromator ( $\lambda = 1.5418\text{ \AA}$ ) at a scanning rate  $0.04^\circ/\text{s}$  from  $5^\circ$  to  $50^\circ$ .

### 2.2. Crystal structure determination

Crystallographic data were collected at 293(2) K with a Siemens SMART CCD diffractometer using graphite-monochromated (Mo  $K\alpha$ ) radiation ( $\lambda = 0.71073\text{ \AA}$ ),  $\psi$  and  $\omega$  scans mode. The structures were solved by direct methods and refined by Full-Matrix least-squares on  $F^2$  method. Intensity data were corrected for Lorenz and polarization effects and a multi-scan absorption correction was performed. All non-hydrogen atoms were refined anisotropically. The carbon-bound hydrogen atoms of all the complexes were added geometrically. The oxygen-bound hydrogen atoms of water molecules were located in the difference Fourier map and then kept fixed in that position. The contribution of these hydrogen atoms was included in the structure factor calculations. Two oxygen atoms (O4W and O5W) of lattice water molecules in **1** were disordered over two positions. All calculations were carried out on a PC computer using SHELXL-97 program [21]. Details of crystal data, collection, and refinement are listed in Table 1.

### 2.3. Synthesis of $[\text{Cd}(\text{ATIBDC})(\text{btb})(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ (**1**)

A mixture of  $\text{H}_2\text{ATIBDC}$  (0.056 g, 0.100 mmol) and NaOH (0.4 ml, 0.5 mol/l) was dissolved in water (5 ml) and then an aqueous solution of  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  (0.046 g, 0.200 mmol) was added while stirring. To this solution btb (0.019 g, 0.100 mmol) in water (5 ml) was added and then filtered. Pale yellow polyhedral crystals were collected (61% based on  $\text{H}_2\text{ATIBDC}$ ). *Anal. Calc.* for  $\text{C}_{16}\text{H}_{24}\text{CdI}_3\text{N}_7\text{O}_9$ : C, 20.20; H, 2.54; N, 10.30. Found: C, 20.11; H, 2.47; N, 10.21%.

### 2.4. Synthesis of $[\text{Zn}(\text{ATIBDC})(\text{btb})] \cdot 2\text{H}_2\text{O}$ (**2**)

Complex **2** can be obtained following the same synthetic procedure as that for **1** except that  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.060 g, 0.200 mmol),

**Table 1**  
Crystal data and structure refinement for the complexes **1–2**.

	<b>1</b>	<b>2</b>
Empirical formula	$\text{C}_{16}\text{H}_{24}\text{CdI}_3\text{N}_7\text{O}_9$	$\text{C}_{16}\text{H}_{18}\text{I}_3\text{N}_7\text{O}_6\text{Zn}$
Formula weight	951.52	850.44
Temperature (K)	293(2)	296(2)
Wavelength ( $\text{\AA}$ )	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$Pna2_1$
<i>a</i> ( $\text{\AA}$ )	8.1689(4)	16.511(3)
<i>b</i> ( $\text{\AA}$ )	20.2307(9)	14.854(2)
<i>c</i> ( $\text{\AA}$ )	17.2518(8)	10.1159(15)
$\alpha$ ( $^\circ$ )	90	90
$\beta$ ( $^\circ$ )	96.9830(10)	90
$\gamma$ ( $^\circ$ )	90	90
<i>V</i> ( $\text{\AA}^3$ )	2829.9(2)	2480.9(6)
<i>Z</i>	4	4
$D_{\text{calc}}$ ( $\text{mg}/\text{m}^3$ )	2.233	2.277
Absorption coefficient ( $\text{mm}^{-1}$ )	4.099	4.769
$F(0\ 0\ 0)$	1792	1600
$\theta$ range for data collection ( $^\circ$ )	1.56–27.50	1.84–27.42
Index ranges	$-10 \leq h \leq 10$ $-26 \leq k \leq 23$ $-21 \leq l \leq 21$	$-21 \leq h \leq 21$ $-17 \leq k \leq 19$ $-12 \leq l \leq 13$
Reflections collected	17 765	20 561
Unique ( $R_{\text{int}}$ )	6452 [ $R_{\text{int}} = 0.0222$ ]	5466 [ $R_{\text{int}} = 0.0466$ ]
Completeness to $\theta = 27.5$	99.40%	99.60%
Maximum and minimum transmission	0.406 and 0.226	0.424 and 0.249
Goodness-of-fit on $F^2$	1.047	1.066
Final <i>R</i> indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0285$ $wR_2 = 0.0775$	$R_1 = 0.0323$ $wR_2 = 0.0723$
<i>R</i> indices (all data)	$R_1 = 0.0352$ $wR_2 = 0.0809$	$R_1 = 0.0420$ $wR_2 = 0.0879$
Largest different peak and hole ( $\text{e \AA}^{-3}$ )	1.927 and $-1.019$	0.982 and $-0.784$

btb (0.019 g, 0.100 mmol),  $\text{H}_2\text{ATIBDC}$  (0.112 g, 0.200 mmol), and NaOH (0.8 ml, 0.5 mol/l) were used. Pale yellow crystals were formed. Complex **2** loses crystallinity in the open air and turns into the pale yellow powder formulated as  $[\text{Zn}(\text{ATIBDC})(\text{btb})] \cdot \text{H}_2\text{O}$  (**2A**) (44% based on btb). *Anal. Calc.* for  $\text{C}_{16}\text{H}_{18}\text{I}_3\text{N}_7\text{O}_5\text{Zn}$ : C, 23.09; H, 1.94; N, 11.78. Found: C, 22.89; H, 1.89; N, 11.69%.

## 3. Results and discussion

### 3.1. Synthesis of the complexes

The formation of the products is sensitive to synthetic conditions. The hydrothermal method is not suitable for the syntheses of these two complexes since the  $\text{ATIBDC}^{2-}$  ligand decomposes under hydrothermal condition. Therefore, the complexes **1–2** have been obtained under soft ambient conditions. NaOH is used to neutralize the acid. Interestingly, the molar ratio of  $\text{H}_2\text{ATIBDC}:\text{NaOH}$  is important for the formation of **1–2**. The molar ratio of  $\text{H}_2\text{ATIBDC}:\text{NaOH} = 1:2$  was used to synthesize the complexes **1–2**. Otherwise the polycrystals or cotton-like solids were obtained.

Complex **2** loses crystallinity rapidly in the open air, resulting in the formation of the powder  $[\text{Zn}(\text{ATIBDC})(\text{btb})] \cdot \text{H}_2\text{O}$  (**2A**) supported by the elemental and thermogravimetric analysis.

### 3.2. Structure description of $[\text{Cd}(\text{ATIBDC})(\text{btb})(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ (**1**)

Complex **1** crystallizes in monoclinic system with space group  $P2_1/n$ . There are one Cd(II) atom, one  $\text{ATIBDC}^{2-}$  anion, two coordinated water molecules, and three lattice water molecules in the asymmetric unit (Fig. 1A). The Cd(II) lies in a distorted pentagonal bipyramid environment, in which the equatorial plane contains O1, O2, and O3 atoms from two carboxylate groups of two different

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